

the fact that not the whole of the field surrounding the wires lies in the water.

The uncertainty due to this stray field might be easily avoided in one way, namely, by making one wire into a tube surrounding the other and using this tube also as the jar for the electrolyte. This was, in fact, the arrangement originally intended to be adopted. Several disadvantages attended it, however, and led to its final rejection in favour of the simple wires and glass jar. First, such a condenser reflects under all circumstances a considerable portion of the incident energy.\* Secondly, the variation of the position of the top surface of the electrolyte relatively to the top of the jar would introduce fresh interference phenomena. This appeared directly from the work of Mr. Barton to which I have already had occasion to refer. Lastly, the large surface of metal in contact with the liquid would render distilled water rapidly impure.

This investigation was carried out in the Physical Institute of the University of Bonn. I desire particularly to express my thanks to Professor Hertz for his most useful advice and suggestions.

VII. "On the Ratio of the Specific Heats of the Paraffins and their Monohalogen Derivatives." By J. W. CAPSTICK, M.Sc. (Vict.), B.A. (Camb.), Scholar and Coutts-Trotter Student of Trinity College, Cambridge. Communicated by Professor J. J. THOMSON, F.R.S. Received May 25, 1893.

(Abstract.)

The experiments were undertaken to find whether the internal energy of the molecules of organic gases, as deduced from the ratio of the specific heats, showed any regularities corresponding to the chemical resemblances symbolised by the graphic formulæ.

The paraffins and their monohalogen derivatives are very suitable for the purpose, as their chemical relations to each other are simple, they are easily volatile, and are stable enough to be unaffected by ordinary purifying agents.

From the ratio of the specific heats we can calculate the relative rates of increase of the internal energy and the energy of translation of the molecules per degree rise of temperature, and, the aim of the experiments being to compare the rates of increase of the internal energy of different gases, it was decided to keep the translational energy constant by working at a constant temperature. Consequently the determinations were all made at the temperature of the room.

The ratio of the specific heats was calculated from the velocity of

\* J. Ritter von Geitler, Doctor-Dissertation, Bonn, Jan., 1893.

sound in the gases. This was determined by Kundt's method, using a double-ended form of apparatus, in all essential features the same as that described in 'Pogg. Ann.,' vol. 135. The tube in which the dust figures were made was 125 cm. long and 26 mm. in diameter, which Kundt showed to be great enough to avoid any lowering of the velocity of sound from the influence of the walls of the tube.

Lycopodium was used for forming the figures in the hydrocarbons and in methyl and ethyl chlorides, but in the heavier gases it became sticky, and would not move readily, so for these silica was used.

To measure the figures a piece of apparatus was constructed, consisting of a pair of parallel platinum wires, carried by a framework which slides along a steel scale graduated to millimetres. The tube was placed on V-shaped supports, parallel to the scale, and between the wires, which were so adjusted that their plane passed through the centre of the nodes. The position of the framework was then read on the scale, tenths of a millimetre being estimated with the help of a lens. With figures of average quality the setting of the wires could be repeated so as to agree within two or three tenths of a millimetre. The greatest divergence of the observed length of any one figure from the mean of the series was usually about five or six tenths of a millimetre.

The calculation of the ratio of the specific heats from the velocity of sound requires the density of the gas to be known, a circumstance which makes the method very sensitive to small amounts of impurity in the material.

Regnault's value of the density was used for methane, and every precaution was taken to secure pure gas. Two methods of preparation were used, Gladstone and Tribe's, by the action of the copper-zinc couple on methyl iodide and alcohol, and Frankland's, by the action of zinc methyl on water. After each experiment an analysis of the gas was made to test its purity and to determine the amount of air present, for which a correction was made.

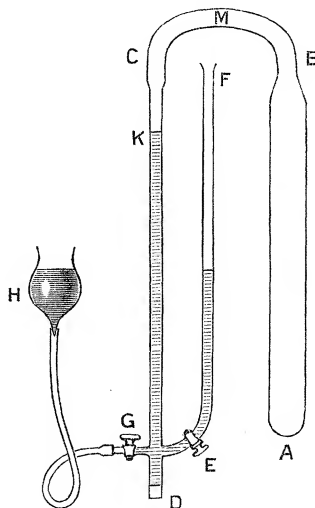
The ethane was prepared by the action of zinc ethyl on water, and for it the theoretical density calculated from the molecular weight was used.

For the preparation of propane, isopropyl iodide was reduced by zinc and hydrochloric acid, and the gas was freed from air by liquefaction in a freezing mixture of ether and solid carbonic acid, after passing through fuming sulphuric acid and potash, and over 30 grams of palladium.

Methyl and ethyl chlorides were prepared in the usual way, by passing hydrochloric acid into a boiling solution of zinc chloride in the corresponding alcohol, and purified by redistillation through suitable reagents. All the rest of the compounds were purchased from Kahlbaum, and were dried and fractionated before being used.

The vapour densities of propane and all the halogen compounds were determined at various pressures for the material as it was used in the velocity of sound experiment, thus avoiding to a great extent any error arising from impurity.

FIG. 1.



The apparatus used for this purpose is shown in fig. 1. Before joining the parts together, the tube CD is calibrated, and after it has been attached, but before the side tubes are fixed on, the volume of the whole is determined by filling with water and weighing. Then, from the calibration of CD, the volume is known between A and a file mark at K.

A weighed quantity of the liquefied gas whose vapour density is required is sealed up in a small tube with capillary ends, and introduced at D, and, by inclining the apparatus, is made to slide over the bend and rest at M. The end D is then closed with a cork, and the apparatus exhausted through the three-way tap G, on the completion of which operation mercury is allowed to flow in from the reservoir H, and the tap E is opened. The difference of the levels of the mercury in the two tubes is read with a cathetometer, and, subtracted from the height of the barometer, gives the pressure of the residual air. On tilting the apparatus, the tube slides over into the wider part, and the end breaks off, allowing the liquid to evaporate. By reading the levels again we get the pressure of the gas, and knowing its weight and volume, we have all the materials required for calculating its specific gravity.

In the experiments the reservoir was always adjusted so that the level of the mercury in CD stood near the mark at K, thus simplifying the calculations a little.

The apparatus was found to give values of the vapour density concordant to about one part in 1000.

The formula used in calculating the ratio of the specific heats was

$$\gamma = 1.408 \times \rho \times \left( \frac{l}{l'} \right)^2 \left( 1 + \frac{1}{p} \frac{d}{dv} (pv) \right),$$

the last factor being added to the ordinary formula to correct for the divergence of the gas from Boyle's Law.

The correction is obtained at once by putting in the equation  $v^2 = -\gamma v^2 \left( \frac{dp}{dv} \right)_t$  the value of  $\left( \frac{dp}{dv} \right)_t$  given by  $\left( \frac{dpv}{dv} \right)_t = p + v \left( \frac{dp}{dv} \right)_t$ .

From the vapour density determinations a curve is constructed giving  $pv$  in terms of  $v$ , and the slope of this curve at any point gives the value of  $\frac{d}{dv} (pv)$  in arbitrary units. Dividing by the corresponding value of  $p$  in the same units, we obtain the amount of the correction.

The correction increases the ratio of the specific heats by from 1 to 2 per cent. in most cases.

Observations varying in number from three to nine were made on each gas, the extreme range of the values being 2 per cent. for marsh gas,  $1\frac{1}{2}$  per cent. for methyl iodide, and 1 per cent., or less, for the rest.

The mean values are shown in the following table:—

Methane .....	CH <sub>4</sub> .....	1.313
Methyl chloride .....	CH <sub>3</sub> Cl .....	1.279
Methyl bromide .....	CH <sub>3</sub> Br .....	1.274
Methyl iodide .....	CH <sub>3</sub> I .....	1.286
Ethane .....	C <sub>2</sub> H <sub>6</sub> .....	1.182
Ethyl chloride .....	C <sub>2</sub> H <sub>5</sub> Cl .....	1.187
Ethyl bromide .....	C <sub>2</sub> H <sub>5</sub> Br .....	1.188
Propane .....	C <sub>3</sub> H <sub>8</sub> .....	1.130
Normal propyl chloride ....	nC <sub>3</sub> H <sub>7</sub> Cl .....	1.126
Isopropyl chloride .....	iC <sub>3</sub> H <sub>7</sub> Cl .....	1.127
Isopropyl bromide .....	iC <sub>3</sub> H <sub>7</sub> Br .....	1.131

From this table we have the interesting result that the gases fall into four groups, the members of any one group having within the limits of experimental error the same ratio of the specific heats.

These groups are—

- I. Methane.
- II. The three methyl compounds.
- III. Ethane and its derivatives.
- IV. Propane and its derivatives.

If the members of a group have the same ratio of the specific heats, we know, from a well-known equation in the kinetic theory of gases, that the ratio of the internal energy absorbed by the molecule to the total energy absorbed, per degree rise of temperature, is the same for all. Hence we have the result that, with the single exception of marsh gas, the compounds with similar formulæ have the same energy-absorbing power, a result which supplies a link of a kind much needed to connect the graphic formula of a gas with the dynamical properties of its molecules.

From the conclusion we have reached, it follows with a high degree of probability that the atoms which can be interchanged without effect on the ratio of the specific heats have themselves the same energy-absorbing power, their mass and other special peculiarities being of no consequence. Further, the anomalous behaviour of methane confirms what was clear from previous determinations, namely, that the number of atoms in the molecule is not in itself sufficient to fix the distribution of energy, and suggests that perhaps the configuration is the sole determining cause.

If this is so, it follows that ethane and propane have the same configuration as their monohalogen derivatives, but that methane differs from the methyl compounds, a conclusion that in no way conflicts with the symmetry of the graphic formulæ of methane and its derivatives, for this is a symmetry of reactions, not of form.

# VIII. "On Operators in Physical Mathematics. Part II." By OLIVER HEAVISIDE, F.R.S. Received June 8, 1893.

*Algebraical Harmonization of the Forms of the Fundamental Bessel Function in Ascending and Descending Series by means of the Generalized Exponential.*

27. As promised in § 22, Part I ('Roy. Soc. Proc.,' vol. 52, p. 504), I will now first show how the formulæ for the Fourier-Bessel function in rising and descending powers of the variable may be algebraically harmonized, without analytical operations. The algebraical conversion is to be effected by means of the generalized exponential theorem, § 20. It was, indeed, used in § 22 to generalize the ascending form of the function in question; but that use was analytical. At present it is to be algebraical only. Thus, let

FIG. 1.

